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College of Mineral Industries

THE PENNSYLVANIA STATE UNIVERSITY

TECHNICAL REPORT NUMBER 9

CONTRACT NUMBER Nonr-656(20)
(Metallurgy Branch)

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STEPWISE REVERSAL TRANSFORMATIONS
OF
COESITE AND STISHOVITE

Frank Dachille, Robert J. Zeto and Rustum Roy

December 30, 1962

University Park, Pennsylvania

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The phase equilibria among the many SiO_2 polymorphs long have been of practical and theoretical interest, providing as they do a substantial foundation for the study of structural and chemical aspects of the silicates. With the recent discovery of the new rutile structure polymorph, stishovite, the importance of the system is further enhanced. The p-t equilibrium stability fields of coesite and stishovite are indicated in Fig. 1.

The aspect of the relations among the polymorphs that is of greatest concern here deals with the structural control of the mechanism of transformation of one phase into another.

In all the reconstructive transformations among the silica minerals it has long been assumed that a short range order (SRO) intermediate phase is formed as the first step. Recent data[1] substantiate this idea. In spite of the existence of the SRO intermediate step it is clear however, that structural control derived from the parent structure is still a reality. While Ostwald's stepwise rule may have constituted an over-generalization, its fundamental validity is rooted in the transmissal of structural inheritance in a direct manner via epitaxy or topotaxy, or in a more indirect

manner through an SRO intermediate.

With the increasing use of coesite and stishovite[2] (the high pressure forms of SiO_2) as indicators of meteorite impact, it is essential to know the conditions under which these phases would revert to other forms of SiO_2, and the structural controls and kinetics of the various reactions involved.

The present study involved quenching experiments and in situ x-ray methods to follow the mechanisms and kinetics of the reversal of the high pressure phases coesite and stishovite to the various one-atmosphere-state phases of SiO_2.

Coesite

Subsequent to a study of the quartz-coesite equilibrium [3] our attention has been directed to the kinetics of this reaction. In an effort to determine the activation volume for the reverse reaction an attempt was made to determine how long the metastable coesite would persist at atmospheric pressure in air at various temperatures. Such data would also bear on the possible ceramic use of coesite. Coes[4] in his original paper stated that at 1700°C coesite was transformed to cristobalite and silica glass. In the present work samples from two 'large' batches of synthetic coesite were heated at various temperatures for varying lengths of time, and examined optically and by x-ray diffraction. It has been found that at temperatures from

1100 to 1350°C, coesite apparently transforms to quartz, and the quartz formed then transforms to cristobalite. We have here evidence for the metastable formation of quartz in the range of stability of a less dense polymorph. In the case of the $Li_2O-Al_2O_3-SiO_2$ system[5], the formation of quartz in a few seconds below 870°C and its subsequent persistence above this temperature gives rise to a similar **apparent** phenomenon but this possibility is ruled out on the present work since the coesite does not transform at all below 870°C. Furthermore, no solid solutions of quartz are involved here. A few typical runs are summarized in Figure 2 and Table 1. (The run in which tridymite was obtained was the only one among several similar runs). It will be noted that this constitutes to-date the only atmospheric pressure synthesis of quartz in the absence of any mineralizer". The only other way to form quartz from other forms of silica without mineralizers other than small amounts of water is under pressures up to 20 kb at about 500°.

With the use of a high temperature x-ray furnace[6] the unmistakable growth of quartz on heating coesite on heating coesite (~17 microns) at 1150°C was evident in the growth of the quartz (101) diffraction peak in the first 15 minutes at this temperature. At this time the integrated intensities of the quartz (101) and β-cristobalite (111) and the coesite (130) were about 1/2, 2 1/2 and 1/2 times respectively that of the initial coesite (130). Periodic sacnning of these maxima through five hours showed that the β-cristobalite

(111) intensity increased further (to about 5 times) but the coesite and quartz essentially disappeared, coesite the more rapidly.

This rapid growth of cristobalite is noteworthy whether it arises from an SRO phase directly from the coesite or from quartz intermediate. Under dry conditions cristobalite was found to crystallize from silica glass powder only after 1/2-1 hour at 1300°C [7], and from quartz (-325 mesh) we observed no growth by in-situ x-ray methods in 10 hours at 1200°C, and only 5% after an additional 6 hours at 1250°C.

Stishovite

All the experiments were conducted with a natural stishovite[8] sample weighing 20 mg* in all and were limited to static, quench-type runs at different temperatures using platinum envelopes to hold 1-2 mg samples. The data in Table 2 show clearly that the stishovite differs markedly from the coesite in metastable persistence. It withstands exposure to 400-500°C for a few hours, but becomes amorphous to x-rays in less than 5 minutes between 650 and 750°C. At higher temperatures and longer heating times (1/2-18 hours) crystallization of quartz (in the stability field of tridymite) in the presence of the SRO phase is again observed. Although cristobalite is the first to be observed by x-ray diffraction it is barely evident microscopically after 18 hours at 1100°C whereas the quartz appears as well

formed crystals after 2 hours. No evidence of a transient formation of coesite from the much denser stishovite has as yet been found.

In Figure 3, we attempt to summarize schematically some of the results obtained and a probable interpretation. The unanswered question is whether or not the coesite goes directly to quartz, or whether it first forms a "dense", fine grained SRO phase, which then converts to quartz. In the case of stishovite it appears inconceivable that the 6-coordinated rutile structure could avoid the SRO stage and indeed there is direct evidence for its formation and subsequent conversion at low temperatures. The relative amounts of the various phases formed in any particular run might be explained on the basis of the competing reactions stishovite (or coesite) → SRO; SRO → qtz; qtz → SRO, and SRO → crist with widely differing activation energies.

SUMMARY

Very marked differences in the metastable persistence for coesite and stishovite have been demonstrated, the former possibly persisting indefinitely below 1000°C at 1 atm. "dry", the latter decomposing in minutes above 500-600°C to an SRO phase. Quartz has been grown metastably well above its stability field from both coesite, and stishovite, possibly via an SRO phase. The absence of stishovite in

meteor-impact craters cannot be taken as possible evidence that it was not formed. If it has "reversed" in a normal natural enviroment the product would almost certainly be an SRO phase or derivative.

ACKNOWLEDGEMENT

REFERENCES

1. A.C.D. Chaklader and A.L. Roberts, J. Am. Cer. Soc. 44, 35 (1961).

2. S.M. Stishov, S.V. Popova, Geokhimiya No. 10, 837 (1961) (see also C.B. Sclar, A.P. Young, L.C. Carrison and C.M. Schwartz, J. Geophys. 67 4049 (1962).

3. F. Dachille and R. Roy, Zeits. Krist. Bd. 111, 451 (1959).

4. L. Cross, Science <u>118</u>, 131 (1953).

5. R. Roy and E.F. Osborn, Jour. Am. Chem. Soc. <u>71</u>, 2086 (1949).

6. H.A. McKinstry, Ph.D. Dissertation, The Pennsylvania State University, (1960).

7. R. Rieke and K. Endell, Data cited by R.B. Sosman, The Properties of Silica, p. 99, The Chemical Catalog Company, (1927).

8. E.C.T. Chao, J.J. Fahey, J. Littler, E.J. Milton, J. Geophys. Res. <u>67</u> 419 (1962).

9. J.J. Fahey, 1962 Annual Meeting Geol. Soc. America, p. 49a (Abstract).

10. F.R. Boyd and J.L. England, J. Geophys. Res. <u>65</u>, 749, (1960).

FIGURE LEGENDS

Figure 1   The p-t phase diagram for SiO_2 for quenchable phases.
The coesite-quartz fields after Dachille and Roy[3]
and Boyd and England[10]. The coesite-stishovite
fields tentatively determined after the minimum
points of Sclar et al[2], the slope being commensur-
able with the $\Delta H_{(tr)}$ of the 4 to 6 coordination
change for GeO_2 qtz → rutile.

Figure 2   Influence of time and temperature on the alteration
of coesite. Time is plotted on a logarithmic scale.
Solid and dotted filling indicate relative amounts
of quartz, cristobalite and tridymite phases present.
Circle and square points are for separate lots of
concentrated coesite, with grain sizes averaging
8 and 17 microns respectively. The square marked
X represents the average observations during a 5
hour high temperature x-ray study.

Figure 3   Scheme of the most likely reversal paths of coesite
and stishovite.

Table I

Transformation of Coesite* at Atmospheric Pressure

Temp. °C	Time	Product**
750	12 hours	Coesite
850	24 hours	Coesite
1075	24 hours	Coesite
1120	30 minutes	10% Quartz, 90% Coesite
1200	30 minutes	15% Quartz, 85% Coesite
1200	4 hours	55% Coesite, 30% Quartz, 15% Cristobalite
1200	10 hours	15% Coesite, 30% Quartz, 55% Cristobalite
1250	2 minutes	5% Quartz, 50% Coesite
1250	60 minutes	10% Quartz, 90% Coesite
1300	15 minutes	75% Coesite, 20% Quartz, 5% Cristobalite -
1300	30 minutes	50% Coesite, 25% Quartz, 29% Cristobalite
1300	60 minutes	25% Coesite, 25% Quartz, 50% Cristobalite
1300	24 hours	25% Cristobalite, 75% Tridymite
1300	100 hours	100% Cristobalite

*The coesite was obtained from a number of runs in uniaxial apparatus which were combined and then cleaned by 5% HF washes. Spectroscopic analysis Ni, 0.2%; Pt, 0.1%; Fe, trace; no other elements detected.

**Amounts are very roughly estimated from powder x-ray pattern. The percentage converted may be a function of particle size and previous treatment of the starting material.

Table II

Atmospheric Heat Treatment of Stishovite

Temp.	Time (Hrs.)	X-ray	Results Microscope	Bulk Color
1100	18	Cr. + Qz.	Qz. + Amorph. + Cr.	White
1100	2	Cr. + Qz.	Qz. + Amorph. + Cr.	White
1060	0.5	Cr.	Amorph. (n=1.456)	White
1040	0.1	Amorph.	Amorph. (n=1.456)	White
750	o.1	Amorph.	Amorph.[a]	White
750	0.2	Amorph.	Amorph.	White
650	0.2	Weak Stish.	Stish. + Amorph.[b]	Grey-White
500	0.2	Stish.	Stish.	Grey
425	3.5	Stish.	Stish.	Grey
350	0.2	Stish.	Stish.	Grey
130	0.5	Stish.	Stish.	Grey
900	6.0	Crist. (2)	(From synthetic material)	
500	?	Amorph. (9)	(From natural material)	

a) Apparent index of very fine grained aggregate = 1.48
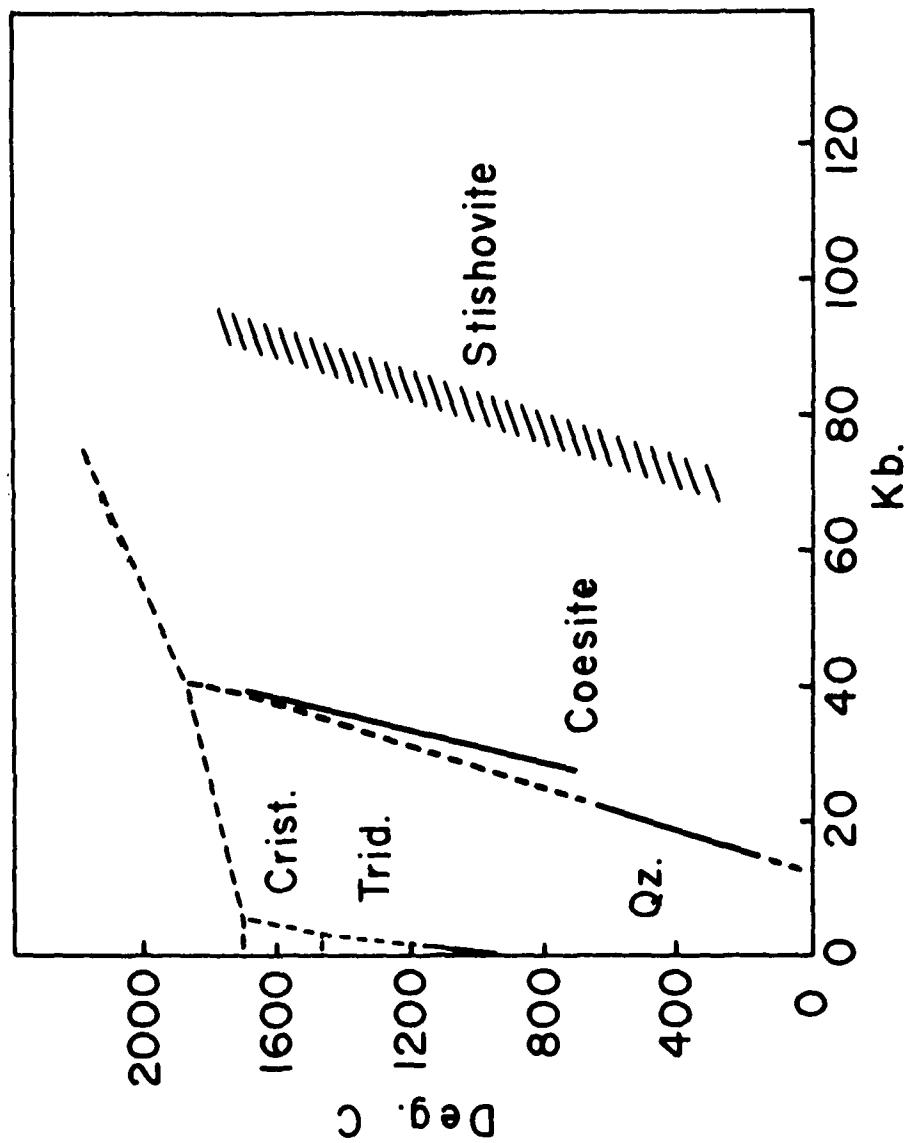
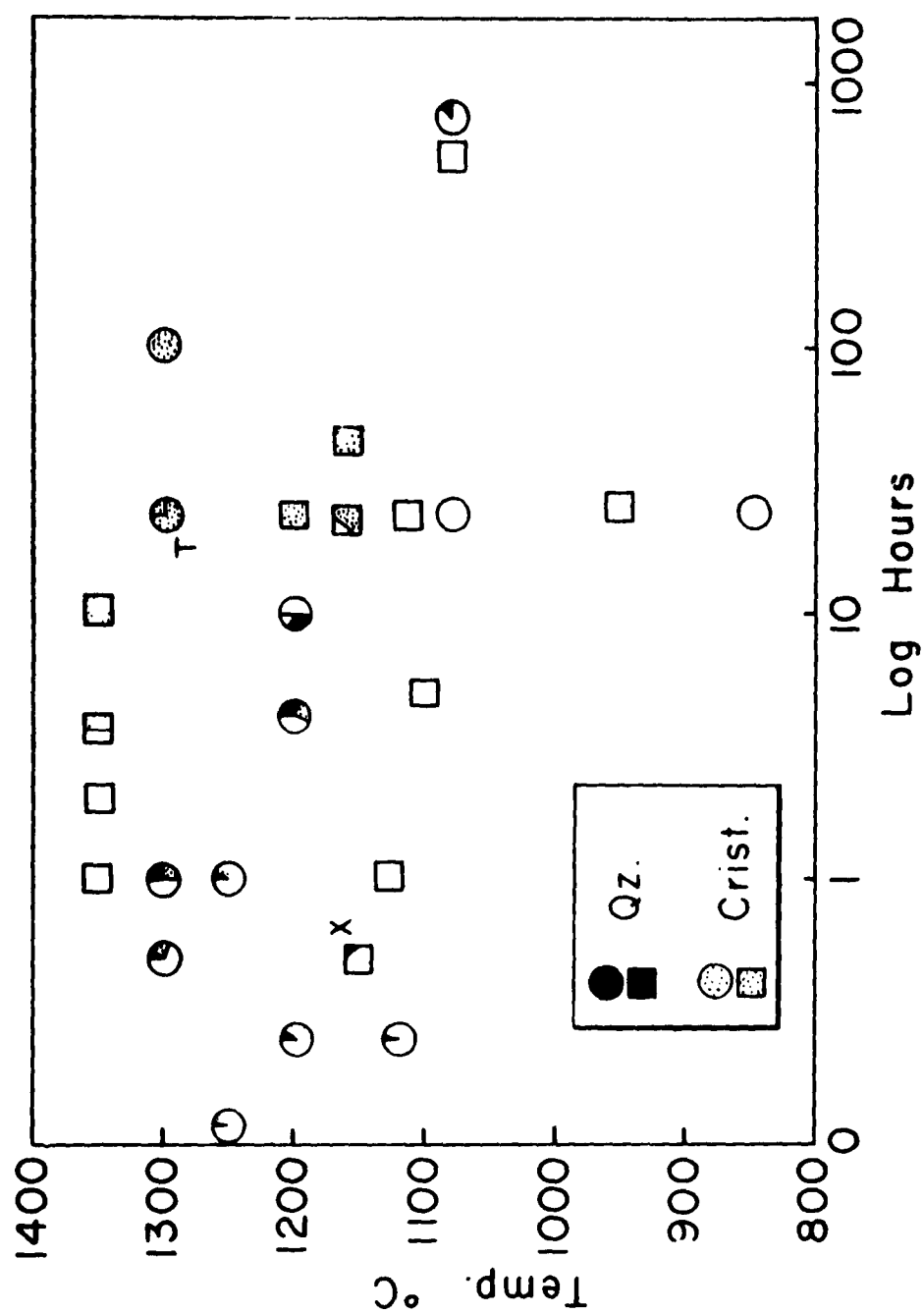b) Apparent index of very fine grained aggregate = 1.50
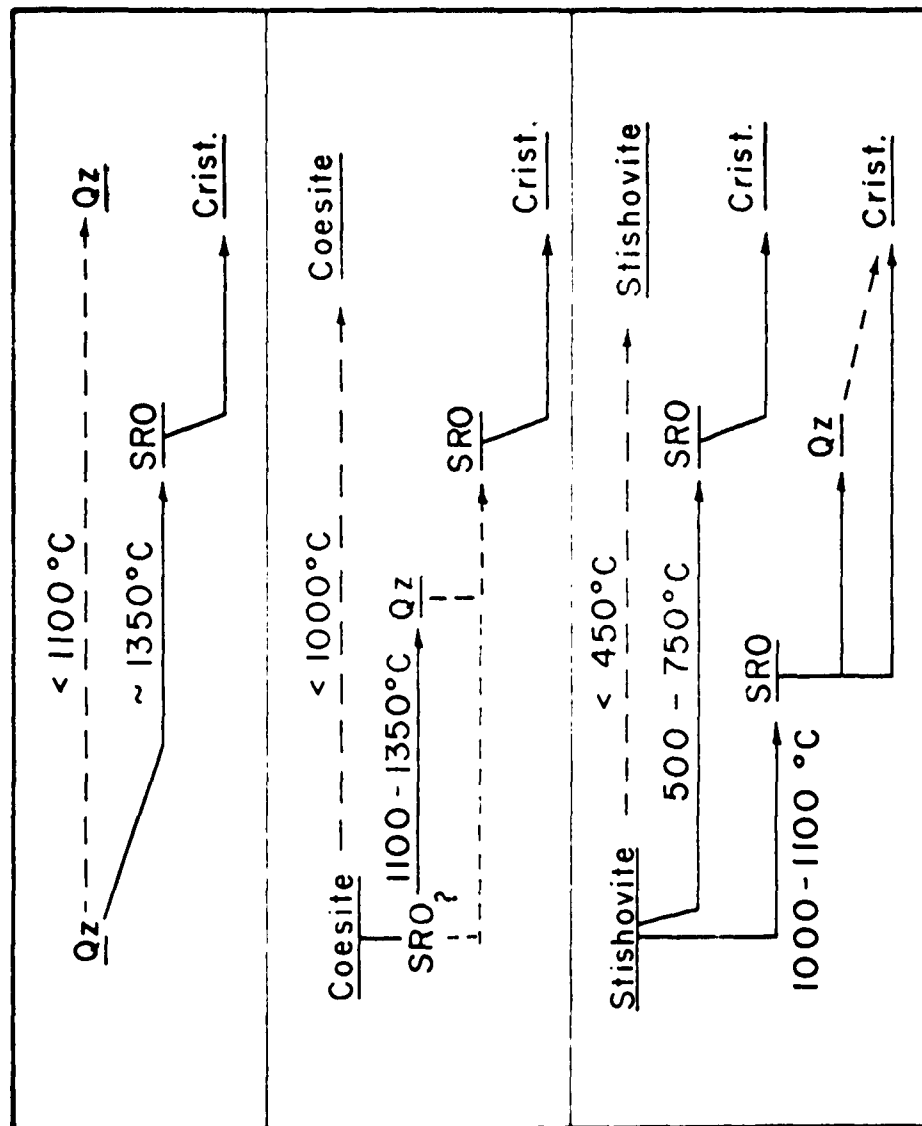
Figure 1

Figure 2

Figure 3.